

STUDIES ON THE OXIDATION OF HEXAMETHYLBENZENE, II;

PREPARATION OF DIMETHYLPYROMELLITIC ACID

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16. Abstract <p>Hexamethylbenzene (HMB) was difficult to be oxidized with an alkaline potassium permanganate solution, since HMB was insoluble in an aqueous alkaline solution. But, when HMB was warmed with 50% nitric acid for a short time, and then treated with aqueous potassium permanganate, the reaction occurred readily and dimethylpyromellitic acid was obtained. When HMB was warmed with 50% nitric acid for 1~2 minutes, a yellow material was produced, which was soluble in hot aqueous potassium hydroxide, though free from carboxylic acids. It contained a little amount of bis-(nitromethyl)prehnitene and several unknown compounds.</p> <p>Further, the heat-stability of polyimide prepared by the reaction of tetramethyldimethylpyromellitate with 4,4'-diaminodiphenylmethane turned out to be nearly equal to that of polyimide prepared from tetramethylpyromellitate.</p>			
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STUDIES ON THE OXIDATION OF HEXAMETHYLBENZENE, II;
SYNTHESIS OF DIMETHYLPYROMELLITIC ACID

(received 17 March 1973)

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Hexamethylbenzene, even when heated in solution with alkaline potassium permanganate, reacts very slowly, but it was found that if the yellow substance obtained by heating for 1-2 minutes with 50% nitric acid is processed in alkaline potassium permanganate solution, the reaction proceeds readily, and dimethylpyromellitic acid is produced. The yellow substance obtained by preprocessing with nitric acid does not contain carboxylic acids, but when heated it is soluble in a potassium hydroxide solution, and it was found to contain a small amount of bis-(nitromethyl)prenitene and various unidentified substances. Furthermore, tetramethyldimethylpyromellitic acid and 4,4'-diaminodiphenylmethane produced a polyimide. This substance exhibited as great or greater heat resistance as the polyimide produced in nearly the same manner from tetramethylpyromellitic acid.

1. INTRODUCTION

Previously the authors, with the intention of employing heavy aromatic hydrocarbons, oxidized hexamethylbenzene (abbreviated to "HMB" in the following) with nitric acid. As a result, it was difficult to produce dimethylbenzene tetracarboxylic acids, and the reaction first yielded a nitrate such as bis-(nitromethyl)prenitene from the HMB and nitric acid, and it is assumed that this was converted to tetramethylbenzenedicarboxylic acids. On the other hand, it has been reported³⁾ that when HMB is oxidized by potassium permanganate, benzene hexacarboxylic acid is produced, but since this has not been explained in detail, in the present report, first the HMB was oxidized by alkaline potassium permanganate, then the reaction products were examined. Next the insoluble yellow substance obtained by heating HMB in 50% nitric acid for a short period of time was oxidized in alkaline

1) This is referenced as "(Second) Report on Research on Oxidation of Hexamethylbenzene".

2) Previous report: (First report), Koji CHIBA, Shin'ya TOMURA, Yoshiyuki MIZUNO, J.Chem.Jour. 1973, 1959.

3) F. Crafts, Ann. Chem., 6, 470 (1884).

potassium permanganate, and dimethylpyromellitic acid was separated from the reaction mixture. Polimides were synthesized from the tetramethyldimethylpyromellitic acid and 4,4'-diaminodiphenylmethane obtained in this manner, and this is reported in the following.

2. THE EXPERIMENT AND REAGENTS

2.1 Raw Materials and Reagents

HMB, as previously reported²⁾, was synthesized by a gas-phase contact reaction of methanol and phenol in the presence of an active alumina catalyst. Diazomethane was prepared by the usual method from nitrosomethyl urea, and for the other reagents high-quality commercial reagents in ether solutions were used. The trimethyl 1,2,4-trimethylbenzenetricarboxylic acid detected by gas chromatography, as previously reported²⁾, was separated, purified and used, and the bis-(nitromethyl) prenitene as previously reported was synthesized from HMB and benzoyl-nitrate.

2.2 Oxidation by Potassium Permanganate

2.0 gm of HMB was dissolved in 10 ml of benzene, and along with an alkaline potassium permanganate solution (5.2 gm of KMnO_4 , and 1.2 gm/100 ml of KOH) this was circulated for 24 hours over a bath. After the benzene was removed, a small quantity of methanol was added, the unreacted potassium permanganate removed, the insoluble part [1] was filtered, and the filtered liquid was adjusted with nitric acid to pH 8. 10.0 gm of silver nitrate dissolved in a small quantity of water was added to this solution, and it was then heated for 30 minutes at 80°C. The precipitate was filtered, and after vacuum drying, suspended in 30 ml of benzene, and this was circulated for 6 hours with 3.0 gm of methyl iodide. After cooling, this was filtered, and the medium was removed from the filtered liquid, leaving 0.5 gm of colorless needle-shaped crystals (yield of hexamethylbenzenehexacarboxylic acid: 9.3 mol %). A gas chromatography (column: Silicone DC 550 (20%)/Celite 545 (60-80 mesh) 4 mm x 1 m, column temperature: 215°C, carrier gas: 40 ml/min N_2) shows only a single peak, and the melting point of the substance recrystallized from methanol was 186-187°C, which agrees with the melting point of hexamethylbenzene hexacarboxylate, 187-188°C³⁾. The extraction with benzene from [1]

yielded 1.8 gm of HMB. The preceding experimental results show that the progress of the reaction of the HMB and alkaline potassium permanganate solution is extremely slow, but the yield is almost entirely alkaline benzenhexacarboxylic acid.

2.3 Oxidation of Nitric Acid by Potassium Permanganate

2.3.1 Oxidation Reaction:

2.0 gm of HMB and 30 ml of 50% nitric acid were heated in a bath for 1-2 minutes, HMB was dissolved in this and then immediately water-cooled, then 50 ml of ether was used three times for extraction. The extracted liquid was adequately cleaned washed with water, the water was removed with anhydrous sodium sulfate, then the ether was removed, yielding 1.9 gm of yellow crystals. Gas chromatography (column: Silicone SE-30 (10%)/Celite 545 (80-100 mesh) 4 mm x 1 m, column temperature: 150 °C, carrier gas: 20 ml/min N₂) showed approximately 30% by weight of bis-(nitromethyl)prenitene, and several other peaks were found. The previously obtained yellow crystals were heated and dissolved in a sodium hydroxide solution (KOH 1.2 gm/20 ml water), and 5.2 gm of potassium permanganate was gradually added. The reaction proceeded readily, and the color faded in 10 minutes. Then this was heated for 5 minutes at approximately 80 °C and the insoluble materials were filtered, yielding an alkaline solution of the reactant product. Nitric acid was used to adjust this to pH 8, and in the same manner as described in the preceding paragraph, it was methylesterified with silver chloride. The 1.4 gm of methylester obtained was subjected to gas chromatography, and the gas chromatogram obtained is shown in Fig.1. As a result, Peak 3 is recognized as the main component.

The 0.4 gm of purified bis-(nitromethyl)prenitene obtained in the preceding was heated with a solution of alkaline potassium permanganate (1.2 gm of KMnO₄, 0.4 gm/50 ml of KOH) to approximately 80 °C for half an hour, then the unsoluble materials were filtered, the filtered solution was adjusted with nitric acid to pH 8, and similarly methyl-esterified with silver chloride, yielding 0.6 gm of colorless needle-shaped crystals. Gas chromatography, as in Fig.1 and under nearly the same conditions, identified Peak 3 (tetramethyldimethylpyromellitic acid, 65 mol %), and trimethyl 1,2,4-trimethylbenzenetricarboxylic acid (22 mol%), and pentamethyl toluenepentacarboxylate (8 mol %).

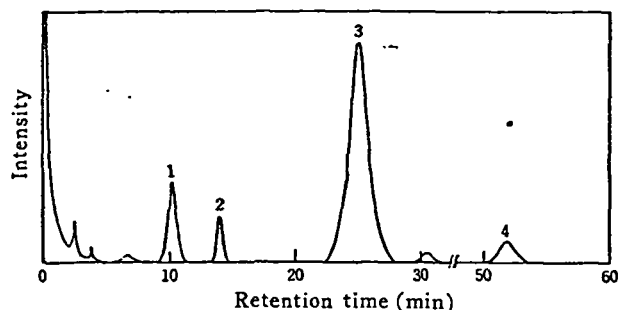


Fig. 1 Gas chromatogram of esterified products (Me-esters)

Column : Silicone DC 550 (20%)/Celite 545 (60~80 mesh)
4 mm×1 m, Temp. : 215°C, Carrier gas : N₂ 40 ml/min,
Detector : FID

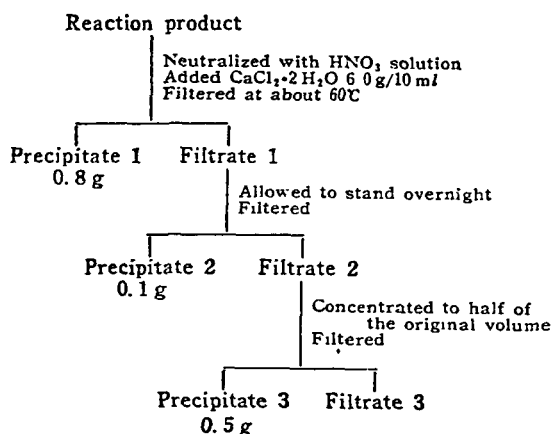


Fig. 2 The separation scheme

2.3.2 Separation of Reaction Products:

The alkaline solution of the reaction product obtained as described in the preceding was processed using the procedure shown in Fig.2. Precipitate 1 was heated along with a 10% sodium carbonate solution, the calcium carbonate produced filtered out, and after the filtered liquid was oxidized with concentrated hydrochloric acid, it was vacuum-dried. Part of this was mixed with about the same quantity of calcium hydrochloride, then heated in an air-circulation oven at 350-400 °C, after which an ether solution of the gas generated was analyzed by gas chromatography (column: Hitachi Gullet column DDP-15 0.25 mm x 15 m, column temperature: 60 °C, carrier gas: 2 ml/min N₂) and a peak matching toluene was found. The vacuum-dried solid corresponds to Peak 4 of the gas chromatogram in Fig.1 of the

substance methylesterified with diazomethane, its retention time is long, and from the fact that toluene by the carbonic acid removal reaction, Precipitate 1 is thought to be the calcium chloride of the toluene pentacarboxylate. For Precipitate 2, an alkaline solution obtained by nearly the same processing was oxidized with hydrochloric acid, and colorless, small needle-shaped crystals (2) were extracted. This part was methylesterified with diazomethane, and by recrystallization from methanol, colorless wheel-shaped crystals with a boiling point of 84-86^oC were obtained. This matches Peak 1 in Fig.1, and its IR spectrum (cm^{-1}) absorbs at the C=O frequency of 1726 and C-O-C frequencies of 1234 and 1126, and the results of elemental analysis agree with the calculation values of trimethyl trimethylbenzene-tricarboxylic acid.

Analytical value:	C 61.01%, H 6.35%
$\text{C}_{15}\text{H}_{18}\text{O}_6$ calculation:	C 61.22%, H 6.16%

Part of [2] was mixed with slaked lime, and as described in the preceding, the reaction of carbonic acid removal is carried out at 300-350^oC, and the results of gas chromatography of an ether solution of the product gas reveals a peak which matches 1,3,5-trimethylbenzene. From this fact it was found that [2] was 1,3,5-trimethylbenzene tricarboxylic acid. After [2] was filtered, the filtered liquid was vacuum-dried, and the substance methylesterified by diazomethane yielded Peaks 1 and 2 on the gas chromatogram of Fig.1, and since Peak 2 matches the previously obtained and reported²⁾ trimethyl 1,2,4-trimethylbenzenetricarboxylic acid, this indicated that Precipitate 2 was a mixture of calcium chloride from 1,3,5- and 1,2,4- trimethylbenzenetricarboxylic acid. After oxidizing Precipitate 3, a similar reaction to remove carbonic acid was carried out at 350-400^oC, and the results of analyzing an ether solution of the product gas by gas chromatography showed that the peak obtained agreed with p-xylene. Part of the previously oxidized substance was methylesterified by diazomethane, and recrystallized from hydrated methanol, yielding colorless needle-shaped crystals [3] with a melting point of 142-143^oC. This substance corresponds to Peak 3 in Fig.1, and its IR spectrum (cm^{-1}) was found to absorb at the C=O frequency 1732 and the C-O-C frequencies 1230 and 1140. The results of

elemental analysis agreed with the calculated values of tetramethyl-
dimethylbenzenetetracarboxylic acid.

Analytical value:	C 56.68%, H 5.26%
$\text{C}_{16}\text{H}_{18}\text{O}_6$ calculation:	C 56.80%, H 5.36%

In the NMR spectrum (δ ppm, CHCl_3), absorption of the CH_3 proton was noted at 2.30, and of the $-\text{OCH}_3$ proton at 3.90, and the fact that the integration ratio was 1:2 indicated that [3] was tetramethyldimethylpyromellitic acid, and thus Precipitate 3 was its calcium carbonate.

However, the repeatability of the separation method shown in Fig.2 was poor. This is probably because these polycarbonates precipitate easily as different potassium and calcium salts according to variations in the conditions, but the details are not clear.

The yield rate of dimethylpyromellitic acid was calculated at 22.1 mol % as the mixture ratio by weight using the relative areas of the peaks on the gas chromatogram in Fig.1.

2.4 Production of Polyimides from Dimethylpyromellitic Acid

Following the method of the patent⁴⁾ of the Dupont Company and using tetramethylpyromellitic acid (TPM), polyimides were produced from tetramethyldimethylpyromellitic acid (TDPM) and 4,4'-diaminodiphenyl methane (DDM).

A powdered mixture of 0.34 gm (1 mmol) of previously prepared TDPM and 0.19 gm (1 mmol) of DDM were placed in a test tube, and the air was replaced by nitrogen. While slowly circulating nitrogen through it, this was heated for 2 hours at 200°C in an oil bath. After air cooling, a brown, glassy reaction product was removed and pulverized, and this was again heated for 2 hours at 275°C in a stream of nitrogen. The IR spectrum of this substance is shown in Fig.3, and the characteristic absorption of polyimides were found at 1775, 1723, 1384 and 750 cm^{-1} . For a thermal balance, the thermal resistance of polyimides produced similarly from TPM and DDM were compared.

4) Japanese Patent Publication 43-13231 [1968]

The results shown in Fig.4 were than polyimides from TPM started to exhibit weight reduction at 335^o C, and the polyimides from TDPM began to exhibit weight reduction at 360^o C. This fact showed that the polyimides from TDPM have an equivalent or greater heat resistance than those from TPM. The TPM used was prepared by the usual method by esterification with ethanol in the present of a sulfuric acid catalyst some pyromellitic anhydride from the Tokyo Chemical Corporation, then recrystallizing from methanol to obtain a substance with a melting point of 141-142^o C.

3 Conclusions

Even when HMB is heated with a solution of potassium permanganate, the reaction is extremely slow, but since a small quantity of the product is benzene hexacarboxylic acid, this is assumed to be due to the fact that HMB is difficult to dissolve. On the other hand, if the HMB is heated for 1-2 minutes with 50% nitric acid, then processed with a solution of alkaline potassium permanganate, the reaction proceeds readily, and dimethylpyromellitic acid is produced. It was found that since the yield of carboxylic acids when processed for a short period with 50% nitric acid is quite minute, the carboxylic acid produced by preprocessing with nitric acid is oxidized by potassium permanganate, yielding dimethylpyromellitic acid. On the other hand, the yellow crystals produced by preprocessing with nitric acid were found to contain bis-(nitromethyl) preniline, and these nitration products were found to contain nitroso-salts as dissolved in alkali, and these should oxidize easily in potassium permanganate, although this is not clear from the extent of the present report. The polyimides produced from TDPM and DDM were found to have an equivalent or greater heat resistance than those from TPM, although it would be premature to discuss the effects of the methyl group based on the present report.

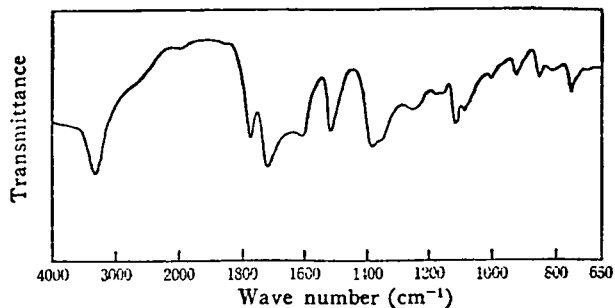


Fig. 3 Infrared spectrum of the polyimide prepared from TDPM and DDM (KBr disk)

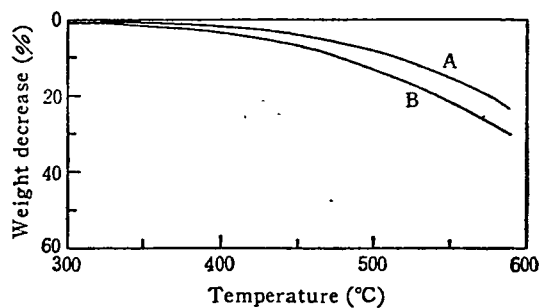


Fig. 4 TGA curves of polymers (5°C/min)
A : Polyimide prepared from TDPM and DDM
B : Polyimide prepared from TPM and DDM

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